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大叶吊兰中一个新的甾体皂甙

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摘要：从百合科植物大叶吊兰（*Chlorophytum malayense*）根茎中分离得到1个新的呋甾烷型甾体皂甙，命名为大叶吊兰甙E（chloromaloside E）。经波谱和化学方法证明其结构为：26－O－β－D－glucopyranosyl－22－hydroxy－25(S)－5α－furostan－12－oxo－3β,26－diol 3－O－β－D－xylopyranosyl(1→3)[α－L－arabinopyranosyl(1→2)]－β－D－glucopyranosyl(1→4)－[α－L－rhamnopyranosyl(1→2)]－β－D－galactopyranoside。同时，还得到大叶吊兰甙A，B和C。

关键词：百合科；大叶吊兰；甾体皂甙；大叶吊兰甙E
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A New Steroidal Saponin from *Chlorophytum malayense*

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Abstract：A new steroidal saponin，named chloromaloside E，was isolated from the fresh rhizomes of *Chlorophytum malayense*，together with three known saponins，chloromaloside A－C. Using the spectral and chemical methods，the structure of chloromaloside E was elucidated as 26－O－β－D－glucopyranosyl－22－hydroxy－25(S)－5α－furostan－12－oxo－3β,26－diol 3－O－β－D－xylopyranosyl(1→3)[α－L－arabinopyranosyl (1→2)]－β－D－glucopyranosyl(1→4)－[α－L－rhamnopyranosyl(1→2)]－β－D－galactopyranoside.

Key words：Liliaceae，*Chlorophytum malayense*，Chloromaloside E，Steroidal saponin

Plants of the superorder Liliaflorae are reported to be rich in steroidal saponins. In recent years，the steroidal saponins have been shown bio－activity，such as antitumor，antimicrobial and cardiovascular system－affecting activity. Earlier，we reported the isolation of four new steroidal saponins chloromaloside A－D from *Chlorophytum malayense* Ridley，a perennial herb of liliaceous plants growing in the tropical regions of southern Yunnan Province，China (Li *et al*，1990a，1990b，1992，1993). In the continuation of work on this plant，we report the isolation and structure elucidation of a new steroidal saponin chloromaloside E (**4**) from the fresh rhizomes of *C*. *malayense* by chemical and spectral methods.

Compound **4** was obtained as colorless needles from MeOH. It was known as a furostane steroidal glycosides by the positive reaction with Ehrlich reagent，and exhibited a molecular formula $C_{61}H_{100}O_{32}$

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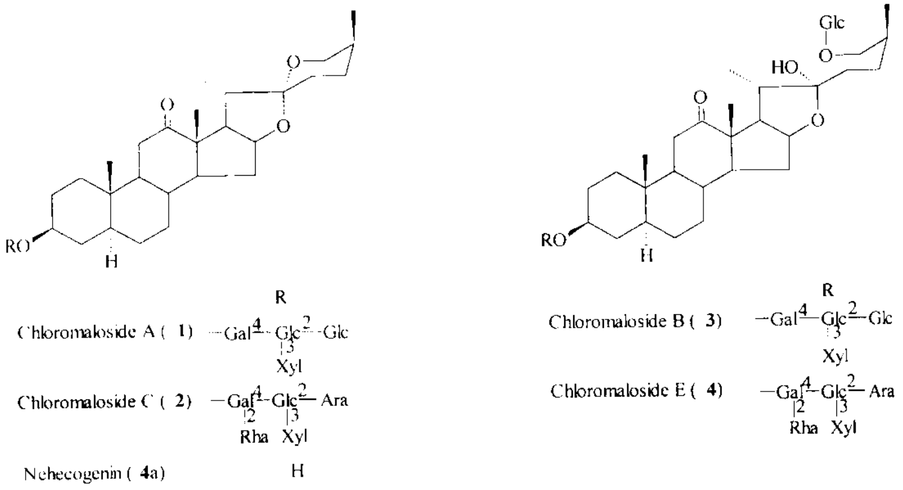
based on its HRFAB and negative FAB mass spectra. A quasimolecular ion $[M-H]^-$ at m/z 1343 was observed. The typical methyl signals of steroidal skeleton at δ 17.56, 16.31, 15.28 and 11.97 in the ^{13}C NMR spectrum and δ1.50 (3H, d, J=6.3Hz), 1.09 (3H, s), 0.99 (3H, d, J=6.4Hz) and 0.85 (3H, s) in the ^{1}H NMR spectrum provided further supporting evidence.

Besides the quasimolecular ion peak, negative FAB mass spectrum gave fragment ions at m/z 1212 ($[M-\text{pentose}]^-$), 1066 ($[M-\text{pentose}-\text{deoxyhexose}]^-$), 918 ($[M-2\text{pentose}-\text{hexose}]^-$) and 772 ($[M-2\text{pentose}-\text{hexose}-\text{deoxyhexose}]^-$), which suggests that the units of pentose, hexose and deoxyhexose were contained in the sugar moiety. Complete hydrolysis of **4** afforded an aglycone, and D-glucose, D-galactose, D-xylose, L-rhamnose and L-arabinose were detected in the hydrolysate. The aglycone was identified as neohecogenin based on the comparison of IR spectrum (Tori *et al*, 1981) and ^{13}C NMR data with those of authentic sample (Li *et al*, 1990).

The structure of sugar moiety was determined based on the comparison of the ^{13}C NMR spectra with that of chloromaloside C. The ^{13}C NMR signals of **4**, due to the sugar moiety, were very similar to those of chloromaloside C, except for a set of additional signals corresponding to a terminal β-D-glucopyranosyl unit. This suggested that **4** contained a terminal β-D-glucopyranosyl unit attached on C-26 position.



Gal: β-D-galactopyranosyl, Glc: β-D-glucopyranosyl, Xyl: β-D-xylopyranosyl
Ara: α-L-arabinopyranosyl, Rha: α-L-rhamnopyranosyl

Structures of compounds 1–4

The sequence and interglycosidic linkages were assigned using a combination of HMBC, HMQC and HMQC-TOCSY experiments. The anomeric proton of β-D-glucopyranosyl H-1 (δ4.85, d, J=7.0Hz) showed cross peak to C-26 (δ75.25), indicating that a glucosyl unit was attached to the C-26 position. It was also observed that there were cross peaks between β-D-galactopyranosyl H-1 (δ4.80, d, J=7.2Hz) and C-3 (δ77.45) of the aglycone, α-L-rhamnopyranosyl H-1 (δ6.25, brs) and β-D-galactopyranosyl C-2 (δ77.45), α-D-glucopyranosyl H-1 (δ5.00, d, J=7.3Hz) and β-D-galactopyranosyl C-4 (δ79.81), α-L-arabinopyranosyl H-1 (δ5.30, d, J=7.2Hz) and β-D-glucopyranosyl C-2 (δ81.49), and between β-D-xylopyranosy H-1 (δ5.19, d, J=6.0Hz) and β-D-glucopyranosyl C-3 (δ88.04) (Fig.1). Thus, the structure of **4** was established as 26-O-β-D-glucopyranosyl-22-hydroxy-25 (S)-5α-furostan-12-oxo-3β, 26-diol 3-O-β-D-xylopyranosyl (1→3) [α-L-arabinopyranosyl(1→2)]-β-D-glucopyranosyl(1→4)-[α-L-rhamnopyranosyl(1→2)]-β-D-galactopyranoside, and named as chloromaloside E. It could be regarded as a biogenetical precursor of chloromaloside C.

Chloromaloside A, B and C were isolated from this crude material and identified based on comparison with authentic samples.

EXPERIMENTAL

^{1}H and ^{13}C NMR (δ, J in Hz) spectra were measured in pyridine-d_5 unless otherwise noted and recorded at 400MHz for 1D-NMR and 500MHz for 2D-NMR with TMS as int. Standard. FAB mass spectra were measured on a VG Autospec mass spectrometer.

Plant material The rhizomes of *C. malayense* Ridley were collected in Xishuangbanna, Yunnan Province, China. The voucher specimen is deposited in the Herbarium of Kunming Institute of Botany, Chinese Academy of Sciences (KUN).

Extraction and isolation Fresh rhizomes of *C. malayense* (126g) were extracted with hot MeOH. The extract was concentrated to almost dryness under reduced pressure. The extracts (30g) were suspended in H_2O and extracted with n-BuOH. The n-BuOH layer was concentrated to dryness to afford a crude saponin (5.2g), which was chromatographed on a silica gel column with $CHCl_3$-MeOH-H_2O (7∶2.5∶0.33) and gave 3 frs. Fr. 1 was chromatographed on silica gel CC with a system of $CHCl_3$-MeOH-H_2O (8∶2∶1, lower layer) and yielded chloromaloside A (1) (20mg). Fr.2 was chromatographed on silica gel CC with a system of $CHCl_3$-MeOH-H_2O (8∶2.2∶1, lower layer) and yielded chloromaloside C (2) (20mg). Fr.3 was chromatographed on silica gel CC with a system of $CHCl_3$-MeOH-H_2O (7∶2∶1, lower layer) to give a mixture. The mixture was subjected to Rp-8 CC column and eluted with 50% MeOH and afforded chloromaloside B (3) (50mg) and compound 4 (140mg).

Chloromaloside E (4) Needles from MeOH. $[\alpha]_D^{20}=-27.4°$ (pyridine, c:0.40). IR $\nu_{max}^{KBr}cm^{-1}$:3410 (brs), 1700 (C=O). HRFAB-MS m/z:1343.6173 ([M ($C_{61}H_{100}O_{32}$)-H]$^-$. Calc:1343.6119). FABMS m/z:1343 ([M-H]$^-$), 1212 ([M-Xyl]$^-$ or [M-Ara]$^-$), 1066 ([M-Xyl-Rha]$^-$ or [M-Ara-Rha]$^-$), 918 ([M-Xyl-Glc-Ara]$^-$), 772 ([M-Xyl-Glc-Ara-Rha]$^-$), ^{1}H NMR (pyridine-d_5):δ 6.25 (1H, brs, Rha:H-1), 5.30 (1H, d, J=7.2Hz, Ara:H-1), 5.19 (1H, d, J=6.4Hz, Xyl:H-1), 5.00 (1H, d, J=7.3Hz, Glc:H-1), 4.85 (1H, d, J=7.0Hz, 26-O-Glc:H-1), 4.80 (1H, d, J=7.2Hz, Gal:H-1), 1.67 (3H, d, J=5.3Hz, Rha:H-6), 1.50 (3H, d, J=6.3Hz, H-21), 1.09 (3H, s, H-19), 0.99 (3H, d, J=6.4Hz, H-27), 0.85 (3H, s, H-18). ^{13}C

NMR data was shown in Table 1 and 2.

Acid hydrolysis of chloromaloside E (4): Compound 4 (100mg) was dissolved in 1mol/L HCl in MeOH－H_2O (1∶1) and refluxed for 2 hours. The reaction mixture was neutralized with $NaHCO_3$ (1mol/L) and extracted with $CHCl_3$ three times. The $CHCl_3$ phase was chromatographed on the silica gel column with $CHCl_3$ and yielded aglycone (4a) (20mg). The water phase was checked on silica gel HPTLC with the system of *n*－BuOH－*i*－PrOH－H_2O (10∶5∶4, homogenous) and anisaldehyde－H_2SO_4 as detecting agent. The D－glucose, D－galactose, L－rhamnose, D－xylose and L－arabinose were detected by comparison with the authentic samples.

Compound 4a: colorless crystal from $CHCl_3$, EI－MS m/z: 430 [M]$^+$, 415, 402, 358, 343, and 139 (100), IR ν_{max}^{KBr} (cm^{-1}): 3531, 1700 (C=O), 980, 919, 890, 849 (intensity 919>890, 25 (S) spirostanol), ^{1}H NMR (Chloroform－d_3): δ1.12 (3H, d, J=7.0Hz, H－21). 1.10 (3H, d, J=7.1Hz, H－27), 1.04 (3H, s, H－18), 0.90 (3H, s, H－19). ^{13}C NMR data was shown in Table 1.

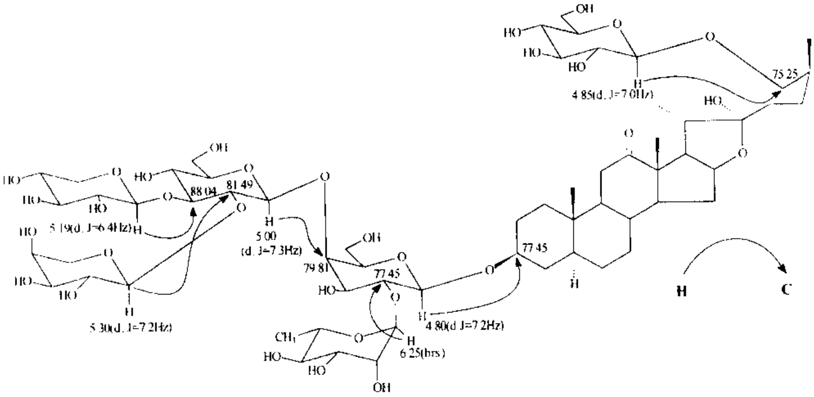


Fig. 1 Key cross peaks of ^{1}H－^{13}C Long－range Correlation of Chlormaloside E (1) in the HMBC spectrum

Table 1 ^{13}C NMR chemincal shifts of aglycone moieties of compounds 1～4 (in C_5D_5N)

C	1	2	3	4	4a*
1	36.77	36.77	36.74	37.12	36.62
2	29.78	29.79	29.75	29.82	31.21
3	77.41	76.96	77.36	77.45	70.89
4	34.77	34.47	34.77	34.77	37.90
5	44.59	44.55	44.62	44.63	44.75
6	28.73	28.71	28.70	28.77	28.33
7	31.84	31.49	31.47	31.81	31.31
8	34.40	34.36	34.48	34.47	34.50
9	55.69	55.66	55.82	55.87	55.74
10	36.41	36.45	36.37	36.51	36.26
11	38.15	38.05	38.03	38.12	38.01
12	213.25	212.81	212.90	213.15	213.45

续表 1

C	1	2	3	4	4a*
13	56.08	55.41	55.62	55.87	55.22
14	55.50	56.00	55.95	55.99	55.89
15	31.84	31.79	31.79	31.81	31.66
16	79.93	79.83	80.01	79.81	79.45
17	54.25	54.24	55.62	55.13	53.52
18	16.43	16.30	16.30	16.31	16.17
19	11.88	11.91	11.82	11.97	12.02
20	43.24	43.19	41.22	41.35	42.85
21	13.92	13.74	15.07	15.28	13.12
22	109.99	109.82	110.86	110.89	109.69
23	26.29	26.48	30.95	30.66	26.12
24	26.51	26.21	28.26	28.40	25.83
25	27.63	27.57	34.48	34.47	27.27
26	65.36	65.25	74.93	75.25	65.24
27	16.26	16.07	17.95	17.56	16.11
22－OCH_3					

* in $CDCl_3$

Table 2　^{13}C NMR chemincal shifts of aglycone moieties of compounds 1～4（in C_5D_5N）

C	1	2	3	4	4a*
Gal	1	102.53	100.29	102.51	100.30
	2	73.24	77.47	73.22	77.45
	3	75.66	76.28	75.64	76.26
	4	79.93	81.41	80.00	79.81
	5	75.45	75.15	75.41	75.14
	6	60.83	60.49	60.75	60.55
Glc	1	105.11	105.36	105.10	105.08
	2	81.38	81.41	81.38	81.49
	3	87.01	88.01	86.89	88.04
	4	70.53	70.44	70.51	70.46
	5	77.64	77.72	77.63	77.67
	6	63.06	62.99	62.95	62.94
Glc（terminal）	1	104.85		104.88	
	2	76.23		76.23	
	3	77.87		77.81	
	4	71.16		71.10	
	5	78.74		78.67	
	6	62.55		62.53	
Rha	1		101.71		101.68
	2		72.42		72.41
	3		72.77		72.76
	4		74.10		74.05
	5		69.10		69.74
	6		18.49		18.52
Xyl	1	105.01	105.01	105.00	105.08

续表 2

C	1	2	3	4	4a*
	2	75.17	75.15	75.12	75.14
	3	78.68	78.77	78.53	78.61
	4	70.87	70.77	70.81	70.78
	5	67.39	67.35	67.37	67.34
Ara	1		105.80		105.77
	2		73.32		73.28
	3		74.74		74.70
	4		69.73		69.34
	5		67.35		67.34
26－O－Glc	1			105.08	105.00
	2			75.26	75.14
	3			78.53	78.61
	4			71.83	71.85
	5			78.67	78.39
	6			62.95	62.94

Chloromaloside A （1） Needles from MeOH，$[\alpha]_D^{20} = -68.5°$ （pyridine，c：0.40），IR，FABMS，and ^{1}H NMR spectra were the same as those of authentic sample. ^{13}C NMR data was shown in Table 1 and 2.

Chloromaloside B （3） Needles from MeOH，$[\alpha]_D^{20} = -31.0°$ （pyridine，c：0.50），IR，FABMS，and ^{1}H NMR spectra were the same as those of authentic sample. ^{13}C NMR data was shown in Table 1 and 2.

Chloromaloside C （2） Needles from MeOH，$[\alpha]_D^{20} = -52.1°$ （pyridine，c：0.50），IR，FABMS，and ^{1}H NMR spectra were the same as those of authentic sample. ^{13}C NMR data was shown in the Table 1 and 2.

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